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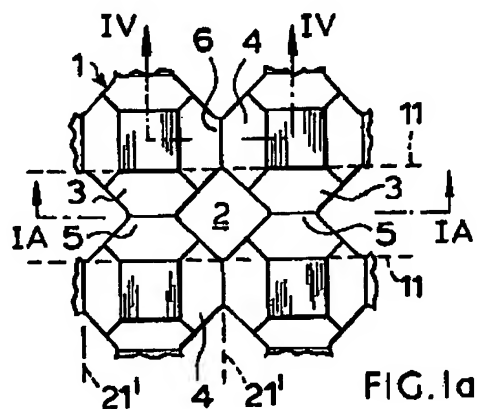
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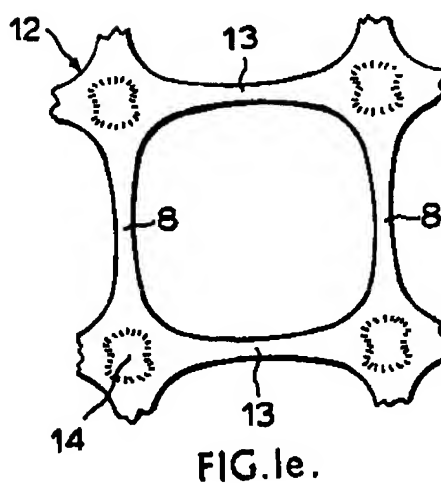
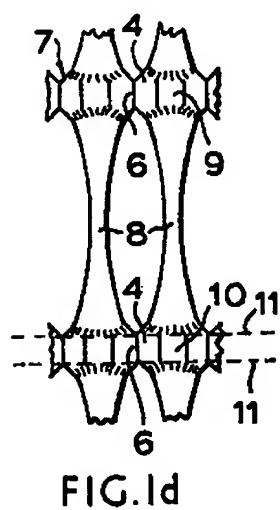
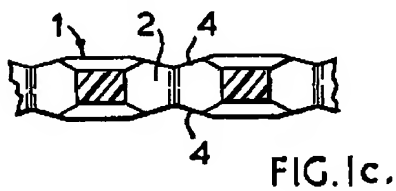
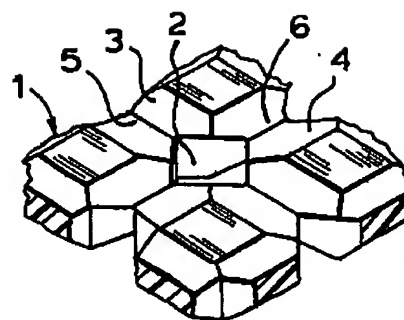
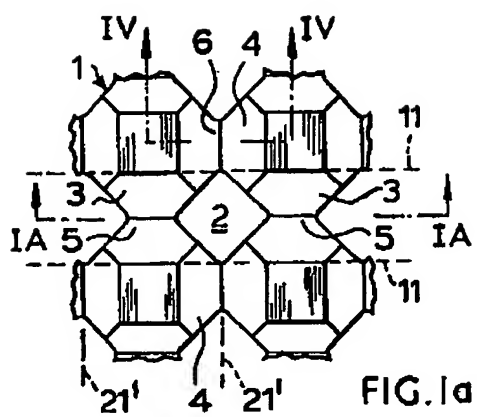
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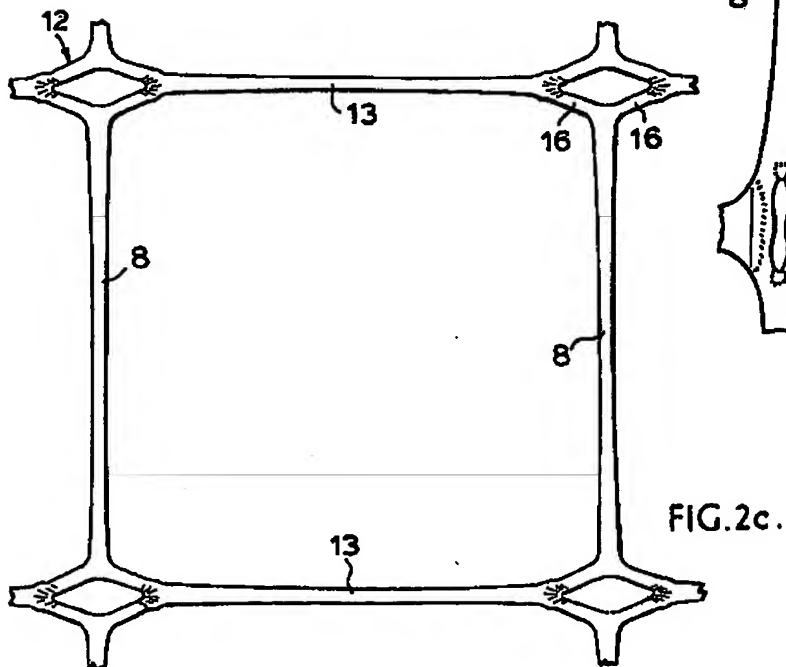
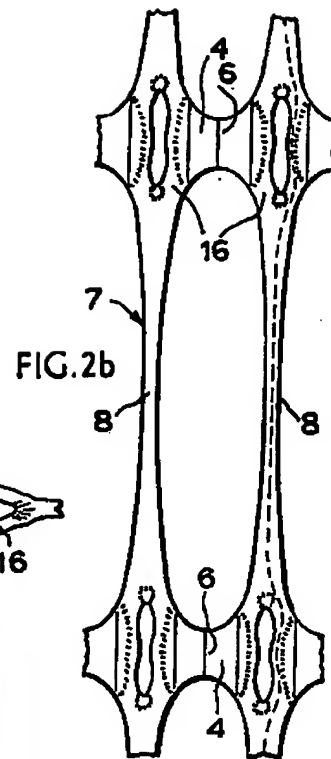
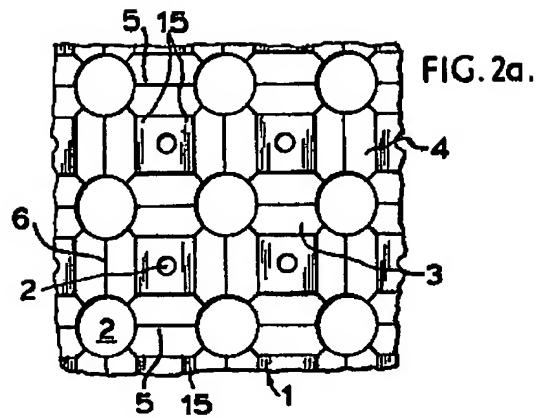
(54) Molecularly orientating plastics material

(57) It is known to form an integral plastics material mesh structure by punching a square or rectangular pattern of holes in a starting material sheet, and then stretching. Particularly when the material is stretched biaxially, irregularities occur across the structure. In order to avoid such irregularities, the strand-forming zones 5,6 are formed with depressions 3,4 with the sheet at a temperature, below the melting range of the material prior to stretching. This is found to greatly improve the regularity, as well as increasing through-put speeds and decreasing power requirements, particularly with polypropylene.



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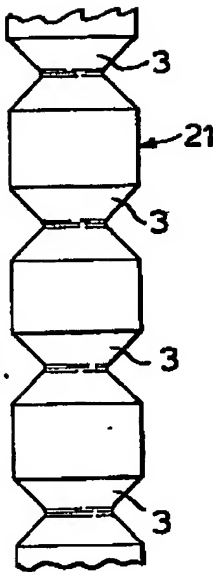


FIG.3a.

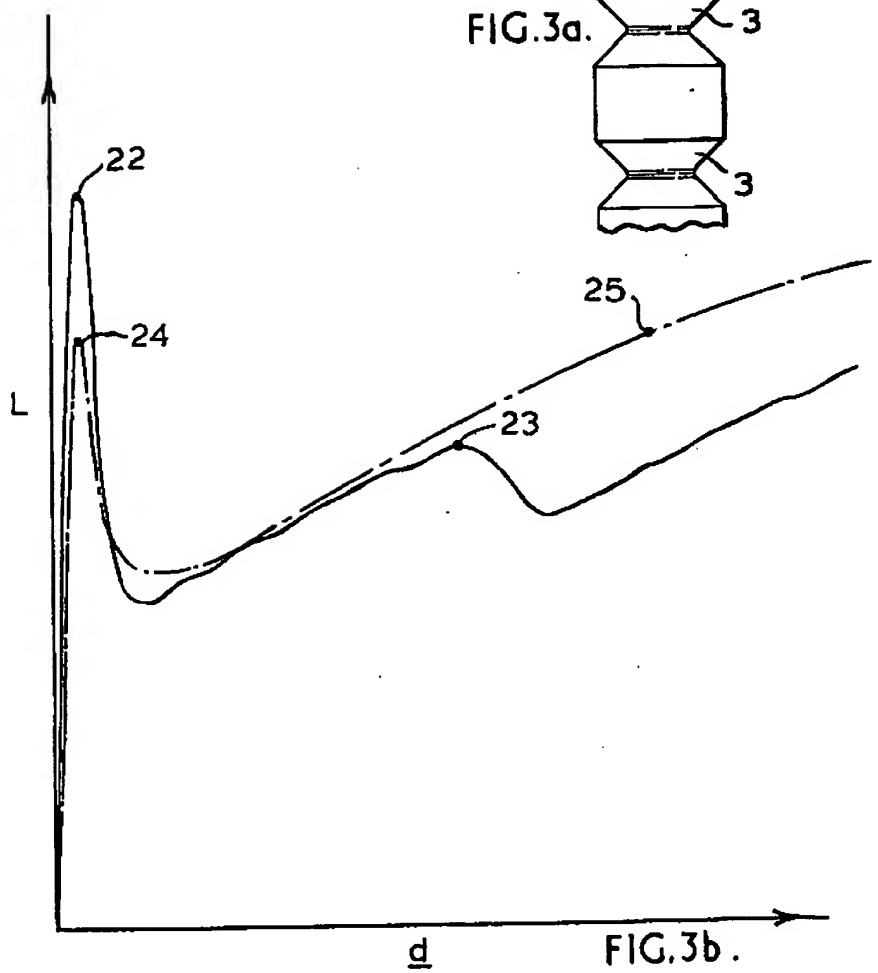
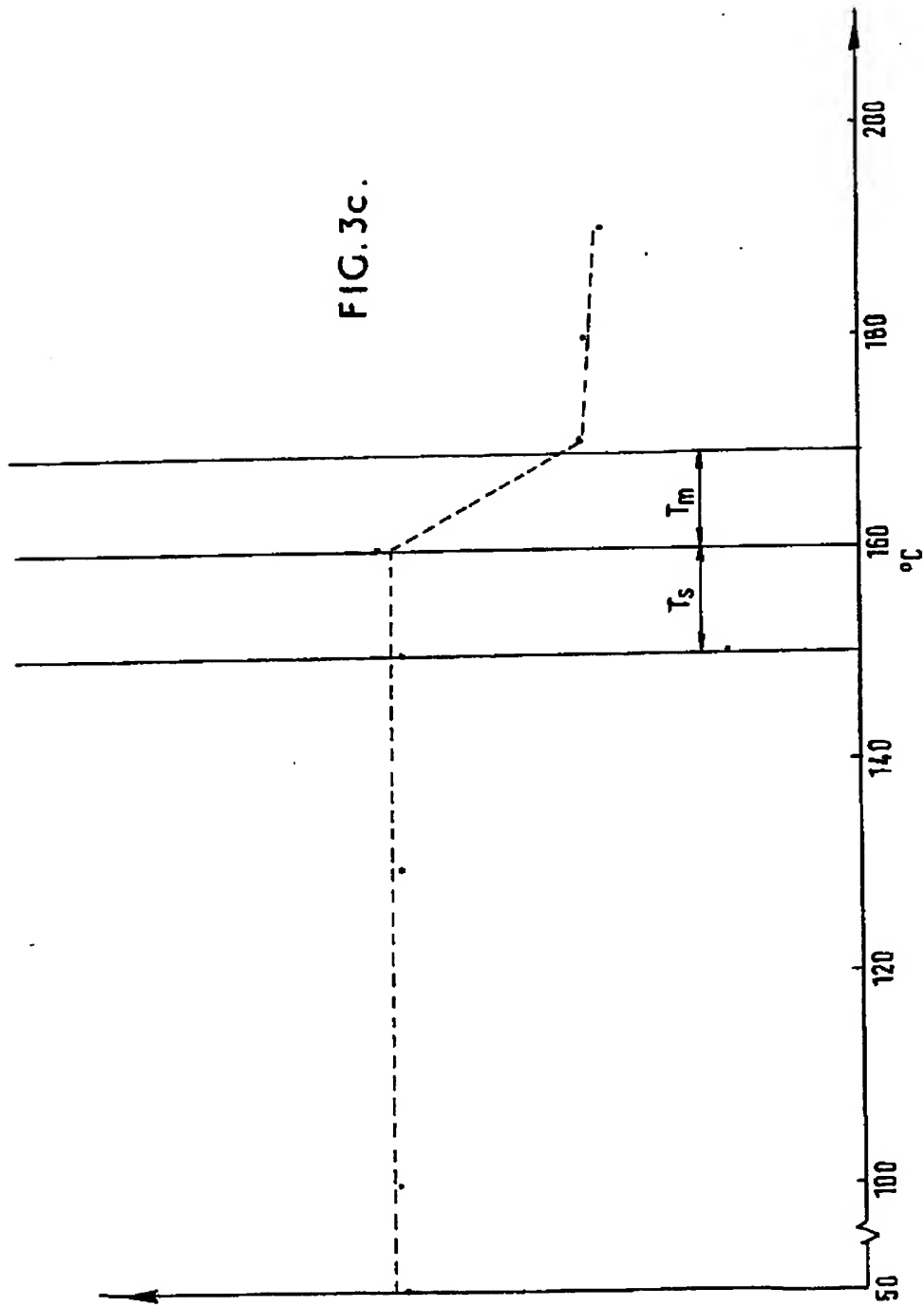
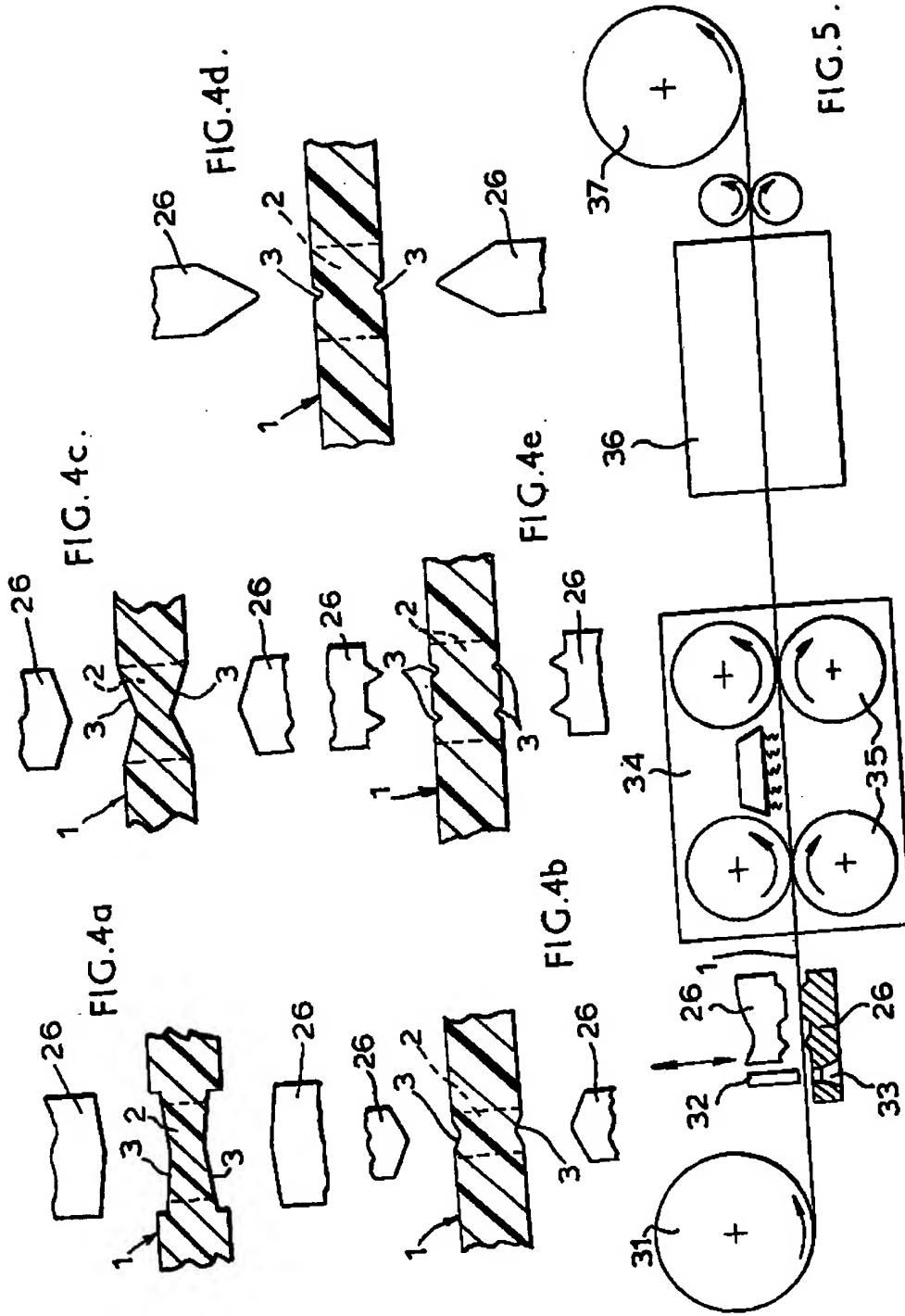


FIG.3b.

FIG. 3c.





SPECIFICATION

Molecularly orientated plastics material

5 *Background of the Invention* 5

The present invention relates to a method of stretching plastics material having a pattern of holes or mesh openings to form molecularly orientated strands from zones (called "strand-forming zones" herein) of the plastics material. In some cases, the whole of the plastics material can be stretched out to form orientated strands. The holes may not penetrate right through the plastics material or the mesh openings may contain membranes, if desired. 10

The method of the invention has been found to be generally applicable, for instance to stretching integrally extruded mesh structures, e.g. those produced as described in GB 836 555, GB 969 655 or GB 1 250 478. The invention is more particularly applicable to methods of producing integral plastics material mesh structures by stretching starting materials having a pattern of holes which can have been formed for instance by punching. Examples of such methods are described in for instance GB 2 031 833A, GB 2 034 240A, GB 2 035 191B, GB 2 059 868A, GB 2 073 090B, GB 2 096 531A, GB 2 108 896A, and GB 82 19477. In all these methods, strands are formed from strand-forming zones of the starting plastics material. Nonetheless, the invention was made in connection with producing biaxially-stretched materials in accordance with GB 2 035 191B, and will mainly be described in relation to GB 2 035 191B, the mesh structure produced being called "biax Square Mesh" herein for convenience. 15 20

The standard way of manufacturing biax Square Mesh is to MD (machine, i.e. longitudinal, direction) stretch using nip rolls, relax 5 to 10%, TD (transverse direction) stretch on a stenter, and relax 5 to 10%. On the stenter, there will be a large number of mesh openings across the width. It was observed that the TD stretching of the mesh openings or TD strands was not regular. As most of the initial increase in width was due to only a few strands stretching, there was very rapid stretching of those strands. In extreme cases, the strands could fibrillate and/or rupture. However, apart from the uneven appearance of the final product, less extreme cases could still cause grave disadvantages; on the first (MD) stretch, a slightly different penetration into the bar or a slightly different amount of penetration across the bar could greatly change the junction formed after the second (TD) stretch: if the increased penetration caused the junction to stretch before the strands in the second stretch, a much weaker and radically different junction would be formed. Similar differences occurred when the second stretch was MD; as the stretch length cannot be very short in practice, there is always a number of aligned strands stretching at the same time. Such differences, though not so marked, were also apparent when making uniaxially-stretched structures. 25 30

In general terms, more difficulties were experienced with polypropylene (PP) than with high density polyethylene (HDPE), but the differences were apparent with HDPE. 35

The Invention

The present invention provides methods as set forth in Claim 1 or 21 and plastics material as set forth in Claim 22. The remaining Claims set forth preferred features of the invention.

It has been found that by forming the depressions without material removal (i.e. without abstracting material from the structure as a whole), a much more regular structure can be formed. In a measurement of the mesh pitches in the TD, after stretching TD in a stenter, a prior PP biax Square Mesh product had a mesh pitch variation (maximum to minimum) of about 45% whereas a biax Square Mesh product in accordance with the invention had a variation of about 5%. In effect, when the strand-forming zones are being stretched in a stenter, there is a controlled, repeatable progression; the orientation usually begins in the lateral zones of the web and gradually works towards the centre, this being related to the natural stress pattern imposed by a stenter; one should apply sufficient stretch to achieve reasonable uniformity. The rate of strain during transverse orientation becomes more regular from mesh to mesh. The effect of this equalising of strain rate can ensure that the tensile strength of all the meshes is nearly the same. 40 45

The reasons for this are not well understood. It is believed that by forming the depression below the melting range, some molecular yielding occurs and there is some pre-orientation of the plastics material in the strand-forming zones, in particular in the deepest part at least of the depression. Microscopic examination under polarised light has indicated some attenuation of the spherulite structure in the direction at right angles to the axis of the depression; there is also some birefringence, signifying some orientation in the same direction. It is believed that the pre-orientation effect is the most important effect. However, there is an indent effect, i.e. predetermining the place where orientation should begin. In addition, the accurate formation of depressions can reduce the variations in thickness which would otherwise occur in the strand-forming zones due to variations in thickness in commercially available plastics material sheets. 50 55

The yield and draw curves are altered, being made much more regular with a lower yield point (yield load); the yield loads can be greatly reduced, particularly for PP. This reduction can be as high as 30%. There is however very little effect on the tensile strength of the final product. It is believed because no plastics material is actually removed and forming the depression has an effect similar to that which occurs on stretching. The cross-sectional size of the strand in the final product is not substantially altered. 60

The invention enables stretching machine power to be reduced because the yield loads are smaller. In addition, as the stretching is more regular and very high strain rates can be eliminated, through-put or 65

overall speed of production can be great. Thus with PP it has been found possible to stretch at a rate of 2000% minute, and starter through-put speeds of 8 metres/minute have been achieved, expected speeds being as high as 20 metres/minute or more.

A greater degree of control of mesh sizes or strand lengths can be effected with PP since the draw load exceeds the yield load at much lower orientation ratios; if it were desired to have a mesh of a smaller size, the range of orientation ratio capable of producing regular structures would allow this to be achieved.

The advantages of forming the depressions to produce improved structures during TD stretching can also be extended to forming the depressions to produce more regular MD stretched material with similar reductions in yield loads and subsequently lower machine power requirements.

All or most plastics materials have no precise melting point: they have a melting range and a softening range, the ranges not being very precisely definable and overlapping. For instance, the softening and melting ranges may be about 118-128°C and 122-138°C for HDPE and 150-160°C and 160-168°C for PP. It is believed that in theory, the depressions could be formed at a temperature close to, e.g. within about 10°C or 15°C of, the lower limit of the melting range. At higher temperatures, material would merely be displaced, in effect reducing the cross-sectional area of, and weakening, the eventual strand. It is more convenient to form the depressions at lower temperatures. In practice, this means that the preferred temperature is at or substantially below the orientation (stretching) temperature (normally about 100°C for HDPE and 110-130°C for PP) or at or close to the ambient temperature, say 15 or 20°C. There is however a danger that some plastics materials, particularly PP, may shatter if depressions are formed rapidly at low temperature, giving a practical lower limit for mass production using e.g. PP; for instance, the depressions could be rolled into PP at 10°C, but it would be advisable to have a minimum temperature of 20°C if the depressions are pressed in at high speed. GB 1 261 151, FR 1 601 073 and GB 900 914 show the formation of depressions or necks, but they are formed in the molten plastics material and the effect of the present invention is not achieved.

It is preferred that the deepest part of the depressions are substantially at the narrowest parts of the strand-forming zones, but this is not essential and great precision is not usually practicable or necessary - for instance there may be a plurality of depressions in a strand-forming zone, spaced in the direction of stretch. As long as the depressions are not in too wide a part of the strand-forming zone, the strand-forming zone will begin to orientate at the depression(s), which is satisfactory.

A wide variety of shapes of depressions can be used, even depressions which do not extend right across the strand-forming zones and are for instance conical. However, the preferred depressions are wedge-shaped, e.g. with the apex of the wedge extending substantially at right angles to the stretching direction; slight radiussing would be applied to the base of the wedge-shaped depression, to stop the tool cutting the plastics material. Alternatively, rounded-section depressions could be used, e.g. a part-circular cylindrical depression with the axis extending substantially at right angles to the stretching direction. In general, with a tool whose cross-section taken parallel to the stretching direction is substantially constant across the width of the tool (direction at right angles to the stretching direction) and presenting opposite, inclined faces in the stretching direction, there is very little movement of the plastics material at right angles to the stretching direction and the orientation caused is most intense at the bottom of the depression. It is preferred that the depressions should extend for the whole length of the holes on either side of the strand-forming zones, though in practice the depressions may be smaller or shorter; the advantage of equating the extent of the depression to the width of the adjacent hole is that on stretching orientation progresses smoothly from the centre of the strand to the junction region. It is possible however to have the depressions bounded by steps substantially at right angles to the faces of the plastics material, the steps also extending at right angles to the stretching direction; this would tend to prevent orientation proceeding beyond the depressions.

The stretching behaviour can be altered by altering the depth of the depressions. It is believed that the depth, rather than the length, of the depression, has the greatest effect.

In practice, the depressions would be formed on the faces of the plastic material. However, at least in theory, it would be possible to form the depressions on the side edges of the strand-forming zones.

The axis of the depression, e.g. the direction in which the base of the wedge extends, is preferably at right angles to the direction in which the strand-forming zone is stretched, or more generally at right angles to the direction of stretch of the starting material as a whole. Thus with a diamond structure such as that of GB 2 034 240A, the axes of the depressions can be at right angles to the direction of stretching the starting material as a whole even though the strand-forming zones extend at an angle to said direction of stretch. Depending on the product to be formed, the axes of the depressions can extend in the TD and/or in the MD.

It is preferred to form the depressions before any stretching, but the strand-forming zones of a second stretch could be formed with depressions after the first stretch.

Some problems would arise because forming the depressions causes a slight increase in MD or TD dimension, possibly 0.5% overall. However, the depressions can be formed by rolling them in, whether in the MD or TD, before or after punching in the case of punched starting materials; pairs of rolls can be used, with the form (corresponding to the depressions) extending around the whole periphery of one or both rolls - this is most suitable for forming MD depressions, and if TD depressions are rolled in, depressions can be formed on the selvages by nipping them with registering (out of mesh) cogs.

Alternatively, the depressions can be formed by straight pressing. The preferred procedure when forming holes in the plastics material by punching, is to press in the depressions during the same press cycle, e.g. as the press ram approaches bottom dead centre; the depressions are thus formed whilst the ram is travelling

at its slowest speed, reducing the possibility of the plastics material being damaged by high impact loads. This can be done for TD and/or MD depressions. The depressions will be formed in a part of the starting material adjacent to the punch and hole.

If there are selvages, it is useful to form the TD depressions in the selvages in addition to the body of the material as this helps the selvages behave in the same way as the remainder of the sheet and not distort the sheet. The selvage would no longer be a wide strip of oriented material of constant thickness but would have an undulating thickness profile with high orientation in the depressed area and a much lower orientation in line with e.g. TD bars. The effect of such a selvage can be three fold. Firstly - by treating the selvage in the same way as the body of the structure the tendency to bow forward in the centre of the web during MD stretching will be greatly reduced. Secondly - the selvage would have the raised sections directly in line with e.g. the TD bar which is to be oriented: therefore on a stenter, the stenter clip would be gripping to maximum effect in the most advantageous position. Lastly - since the raised portions of the selvage would have much less orientation, the tendency for the selvage to split or crack would be much less.

Preferred Embodiments

The invention will be further described, by way of example, with reference to the accompanying drawings, in which:-

Figure 1a is a plan view of a starting material in accordance with the invention;
Figure 1b is an isometric view of the starting material of *Figure 1a*;
Figure 1c is a section along the line I-A-I-A of *Figure 1a*;
Figure 1d is a plan view of the mesh structure formed by stretching the starting material of *Figure 1a* uniaxially (the scale is about half that of *Figures 1a* to *1c*);
Figure 1e is a plan view of the mesh structure formed by stretching the mesh structure of *Figure 1d* along a second axis at right angles;
Figures 2a to *2c* correspond to *Figures 1a*, *1d* and *1e* but show a different starting material and mesh structures;
Figure 3a is a plan view of a test strip;
Figure 3b is a load/extension graph;
Figure 3c is a graph of peak load against depression temperature;
Figures 4a to *4e* show depression shapes, as seen in section along the line IV-IV in *Figure 1a*, on a larger scale; and
Figure 5 is a schematic side view of plant for carrying out the invention.

In the respective *Figures*, the lines ("profile shading") which indicate the profile of the structure extend up and down the slope, following the line of maximum gradient, i.e. at right angles to conventional contour lines.

Figures 1a to 1e

The uniplanar starting material 1 of *Figure 1a* has a pattern of holes 2 whose centres lie on a notional, substantially square or rectangular grid. As shown in *Figure 1a*, depressions 3, 4 are formed by pressure (no material removal) in the strand-forming zones 5, 6 which are to be stretched. The way of stretching the starting material 1 is known and is also explained in GB 2 035 191B. During orientation, the plastics material is maintained approximately at a uniform temperature, a water bath being effective for this purpose as it removes adiabatic heat generated during stretching. In the first stretch, a uniplanar, uniaxially stretched structure 7 (*Figure 1d*) is formed. The stretching force is applied at the same time to a plurality of first strand-forming zones 5 in series; orientation begins at the indents of the strand-forming zones 5 and the zones 5 are stretched out into orientated strands 8 which are interconnected by substantially parallel bars 9. Each bar comprises a succession of alternate notional zones, namely zones 10 between and interconnecting the ends of aligned strands 8 and the second strand-forming zones 6 between the zones 10. As indicated by the profile shading in *Figure 1d*, the orientation of the strands 8 proceeds at least as far as the notional tangent line 11 indicated in *Figures 1a* and *1d*.

In the second stretch, the structure 7 of *Figure 1d* is stretched in a second direction at right angles to form a uniplanar, biaxially-stretched structure 12 (*Figure 1e*). The stretching force is applied to a plurality of the second strand-forming zones 6 in series; orientation begins at the indents of the second zones 6 and the second zones 6 are stretched out into orientated strands 13. The structure 12 is in the form of a generally rectangular grid of orientated strands 8, 13 and orientated junctions 14 therebetween, the profiles of the junctions 14 being indicated by the profile shading.

It will be seen that the holes 2 are radially squares with their diagonals parallel to the stretching directions, defining wedge-shaped indents in the side edges of the strand-forming zones 5, 6; this provides a pronounced indent effect in addition to that of the depressions. An advantage of these holes 2 is that on the first stretch the stress applied to the strands 8 is dispersed and not directed narrowly straight across the bar 9; this causes the distance of penetration of orientation into the bar 9, or the amount of penetration across the bar 9, to be controlled, and in turn causes the penetration to be more regular across the mesh structure 7.

Figures 2a to 2c

These Figures correspond to Figures 1a, 1d and 1e above, modified in accordance with the method of GB 2 098 531A, and need not be described in detail. Figures 2a to 2c illustrate that it is not necessary to form the depressions in all strand-forming zones (though manually all corresponding strand-forming zones would be formed with like depressions). No depressions are specifically formed in the zones 15 that form the short strands or legs 16 though there is some tapering of an edge. The width of the main strand-forming zones 3 is chosen in relation to the width of the zones 15 such that the zones 3 orientate first, when it is found that the zones 15 orientate reasonably regularly.

Figures 3a, 3b and 3c

Test strips 21 were cold profiled at the sides (with material removal) and correspond to a strip down the starting material 1 of Figure 1a between the dashed lines 21' without the depressions 14. The test strips 21 had a maximum width of 16 mm, the remainder of the details being as for Figure 4c below (see Table 2 below), as appropriate. Orientation tests were carried out at 110°C with test strips with planar faces, and with test strips formed at 110°C with the depressions 3, measuring the load (L) against extension (d). The graph of Figure 3b was drawn.

Even with the test strip 21 without the depressions 3 (full line in Figure 3b), some physical change occurs in the strand-forming zones when the load is applied. However, one of the strand-forming zones yields first (point 22 in the graph), orientation occurs and the load decreases. The load then increases in rounded steps to a new maximum 23 (late start to orientation in one or more strand-forming zones), decreases as the further zone(s) begin to orientate, and so on.

When the depressions 3 are present (dash-dot line in Figure 3b), the strand-forming zones all begin to orientate at the same time (point 24, about 20% lower than point 22), and there are no further maxima, a smooth curve being followed. The draw load exceeds the yield load at point 25.

With HDPE, there was little reduction of the yield load (therefore little reduction in power requirements) but the draw curve was smoother, indicating a regular stretching of the meshes in series.

Using the same test pieces 21, depressions were then formed at various temperatures. Orientation was again carried out at 110°C. The tensile tests were then carried out at ambient temperature (20°C). Details of the tests are set out in Table 1 below, and Figure 3c is a graph of the peak load on the product against the temperature at which the depressions were formed. The vertical lines indicate the softening range (T_s) and the melting range (T_m). Below 170°C, the test pieces were heated up in an oven to the temperature specified; however, from 170°C, the depressions 3 had to be formed using a hot grooving tool to heat the plastics material rather than using a hot test piece. In spite of the difference in procedure, there is a clear indication of a change in behaviour over the melting range. This is believed to be the result of flowing material in a molten state away from the centre of the depression, at temperatures of 170°C and above, as opposed to carrying out a small amount of molecular orientation at temperatures of 160°C and below.

TABLE 1

Depressions formed at °C	Orientation Yield Load	Product Peak Load	Strand Tensile Strength N/mm ²
50	124.0	157.5	447
100	125.5	158.2	470
125	125.0	157.5	462
150	133.0	157.0	452
160	120.0	162.0	453
170	138.0	123.0	403
180	135.0	122.0	394
190	130.5	119.0	395

Figures 4a to 4e

Table 2 below gives details of various examples of the depressions 3 of Figures 4a to 4e. Registering depressions 3 of the same depth were formed on opposite faces of 4.5 mm thick PP; the ends of the holes 2 are indicated with dashed lines. The base of each depression 3 is approximately coincident with the centre lines of the holes 2, except for Figure 4e. For different thickness materials, the depressions 3 can be altered proportionally. The tools 28 are indicated; Figure 4b shows that the same tool could be used to make depressions of differing lengths and depths.

TABLE 2 (measurements in millimetres)

	Form	Length of each	Depth of each	Ratio of combined depth to material thickness	Inclination of base facets	Height of step	Pitch of twin	Length of hole	
5									5
	Fig. 4a	10	0.8	26%	3°	0.34	—	8	
10	Fig. 4b	1.8	0.4	18%	26°	—	—	4	10
	Fig. 4b	1.0	0.45	20%	26°	—	—	4	
15	Fig. 4b	2	0.5	22%	26°	—	—	4	15
	Fig. 4b	2.2	0.55	24%	26%	—	—	4	
	Fig. 4c	8	0.55	24%	12°	—	—	8	
20	Fig. 4d	0.52	0.45	20%	60°	—	—	8	20
	Fig. 4e	0.35	0.3	13%	60°	—	4	8	

25 It will be seen that the depressions 3 can be longer than the holes 2 (Figure 4a), shorter than the holes 2 (Figures 4b) or the same length as the holes 2 (Figure 4c). Figures 4d and 4e show that the sides of the depression 3 can be steeper to reduce the force required, and preferred angles are in the range of about 50° to 70°, the end of the tool 26 being radiused to avoid a cutting edge; it is found that the product is substantially the same. Figure 4e shows that more than one depression 3 can be formed in a strand-forming zone 5; if desired, the remote edges of the twin depressions could be aligned with the ends of the hole 2. In one direction, orientation will run along the strand-forming zone 5 until it meets the orientation from the other depression 3 — In the other direction, orientation will pass into or be impeded by the bar 9 or junction 14 in the normal manner.

30 Expressed as a percentage of the thickness of the undepressed zones of the plastics material, the depth of a depression 3 on one face only (i.e. with no registering depression) or the combined depths of registering depressions 3 on opposite faces, is preferably less than about 40%, more preferably less than about 25% the percentage is preferably more than about 10%, possibly more than about 20%.

35 Though only the depressions 3 are illustrated in Figures 4a to 4e, the depressions 4 could be shaped likewise.

40 Figure 5

Figure 5 shows plant for the biaxial stretching of punched plastics material sheet, generally as in GB 2 035 191B. The sheet is unwound from a reel 31 and passed between a line of reciprocating punches 32 and dies 33. The punch beam and the die beam carry tools 26 for forming depressions 3 as in Figure 1a, adjacent the bottom dead centre of the movement of the punch beam. The starting material 1 is then heated in an enclosure 34, stretched MD by differential rolls 35, stretched TD on a stenter in a heated enclosure 36, cooled, and wound on a reel 37. In each direction, the stretching force was applied to a plurality of the strand-forming zones 5,6 at the same time. If desired, the MD stretched material could be cooled and wound on a reel directly after MD stretching, and later unwound for TD stretching.

50 CLAIMS

1. A method of stretching plastics material having holes or mesh openings to form orientated strands from strand-forming zones of the plastics material, and including the step of forming depressions in at least some of the strand-forming zones without material removal when the plastics material is at a temperature below the lower limit of its melting range, prior to stretching the respective strand-forming zones.

2. The method of Claim 1, wherein there is a plurality of the strand-forming zones in series in the stretching direction to which a stretching force is applied at the same time.

3. The method of Claim 1 or 2, wherein said temperature is substantially below the temperature at which the strand-forming zones are stretched.

4. The method of Claim 1 or 2, wherein said temperature is at or close to ambient temperature.

5. The method of any one of the preceding Claims, wherein the depressions are formed with a tool whose cross-section taken parallel to the stretching direction is substantially constant across the width of the tool, and which presents opposite, inclined faces.

6. The method of any one of the preceding Claims, wherein the depressions are wedge-shaped, the apex

of the wedge extending substantially at right angles to the direction in which the respective strand-forming zones are to be stretched.

7. The method of any one of the preceding Claims, wherein a respective depression is in a strand-forming zone between two holes or mesh openings which have the same length in the direction of stretch of the strand-forming zone, the depression extending substantially for the whole length of the holes or mesh openings but not substantially further.

8. The method of any one of Claims 1 to 6, wherein a respective depression is in a strand-forming zone between two holes or mesh openings which have the same length in the direction of stretch of the strand-forming zone, the depression extending for substantially less than the length of the holes or mesh openings.

9. The method of any one of the preceding Claims, wherein the deepest part of a respective depression is substantially at the narrowest part of the strand-forming zone, as measured at right angles to the direction in which the strand-forming zone is to be stretched.

10. The method of any one of the preceding Claims, wherein the depressions are bounded by steps substantially at right angles to the faces of the plastics material, the steps extending substantially at right angles to the direction in which the respective strand-forming zones are to be stretched.

11. The method of any one of the preceding Claims, wherein not more than one depression is formed in a strand-forming zone.

12. The method of any one of Claims 1 to 10, wherein a plurality of depressions, spaced apart in the direction of stretching the respective strand-forming zone, are formed in a strand-forming zone.

13. The method of any one of the preceding Claims, wherein the plastics material is biaxially-stretched in a continuously-operating plant, one stretch being effected in the machine direction and the other stretch being effected in the transverse direction, and the depressions being formed in at least those strand-forming zones which will stretch in the transverse stretch direction.

14. The method of any one of the preceding Claims, wherein the starting material is formed by punching holes in a plastics material sheet, the depressions being formed generally at the same time as the punching in an adjacent part of the starting material.

15. The method of any one of the preceding Claims, wherein the depth of a depression on one face only of the plastics material, or the combined depths if there are registering depressions on opposite faces of the plastics material, expressed as a percentage of the thickness of the undepressed zones of the plastics material, is about 40% or less than 40%.

16. The method of Claim 15, wherein the percentage is about 25% or less than 25%.

17. The method of any one of the preceding Claims, wherein the depth of a depression on one face only of the plastics material, or the combined depth if there are registering depressions on opposite faces of the plastics material, expressed as a percentage of the thickness of the undepressed zones of the plastics material, is about 10% or more than 10%.

18. The method of any one of the preceding Claims, wherein there are registering depressions on opposite faces of the plastics material, and of substantially the same depth.

19. The method of any one of the preceding Claim, wherein, in the side edges of the respective strand-forming zones in which said depressions are to be formed, said holes or mesh openings define wedge-shaped indents.

20. The method of Claim 19, wherein said holes are radiussed squares with a diagonal parallel to the direction in which the respective strand-forming zones are stretched.

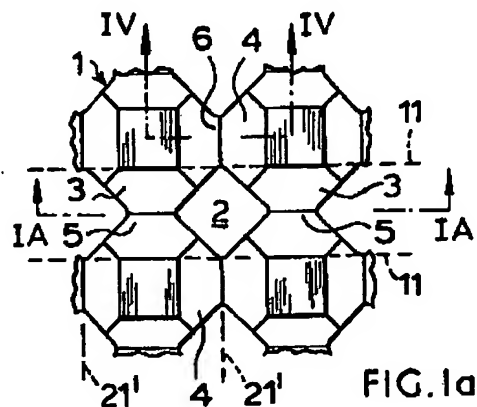
21. A method of stretching plastics material, substantially as herein described with reference to, and as shown, in, any one of Figures 1a to 1d, Figures 2a to 2d, Figure 4a, Figure 4b, Figure 4c, Figure 4d, Figure 4e, or Figure 5 of the accompanying drawings, or with reference to any one of the examples of Table 2.

22. Plastics material which has been stretched by the method of any one of the preceding Claims.

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(54) Molecularly orientating plastics material

(57) It is known to form an integral plastics material mesh structure by punching a square or rectangular pattern of holes in a starting material sheet, and then stretching. Particularly when the material is stretched biaxially, irregularities occur across the structure. In order to avoid such irregularities, the strand-forming zones 5,6 are formed with depressions 3,4 with the sheet at a temperature, below the melting range of the material prior to stretching. This is found to greatly improve the regularity, as well as increasing through-put speeds and decreasing power requirements, particularly with polypropylene.



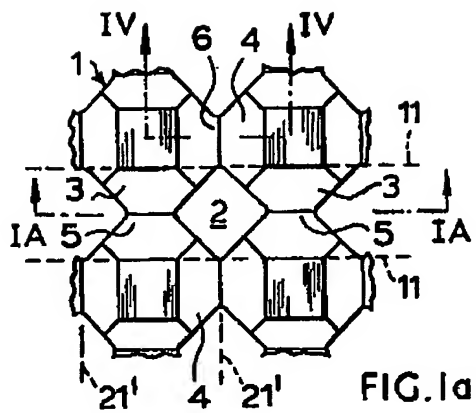


FIG. 1a

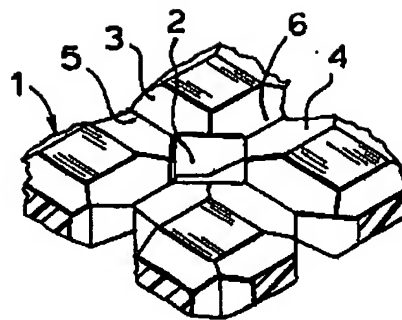


FIG. 1b.

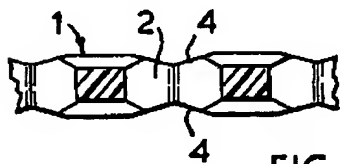


FIG. 1c.

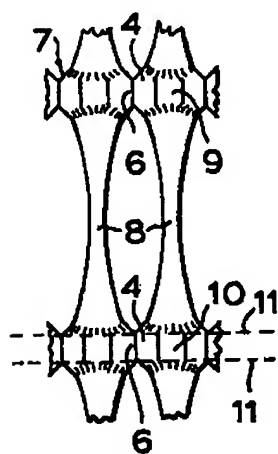


FIG. 1d

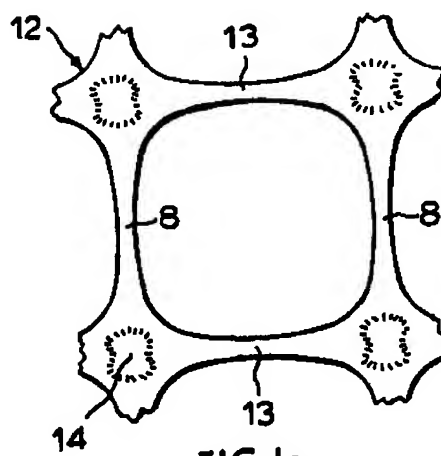
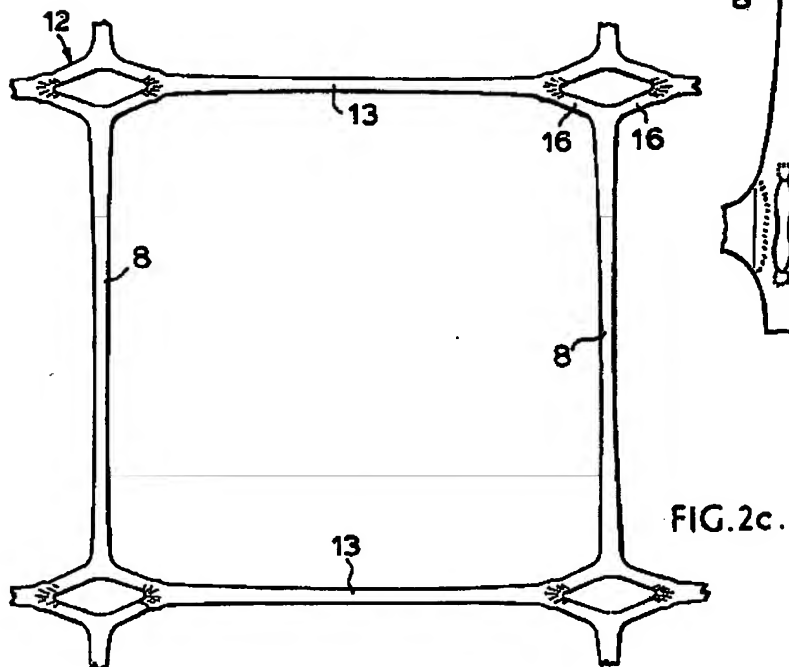
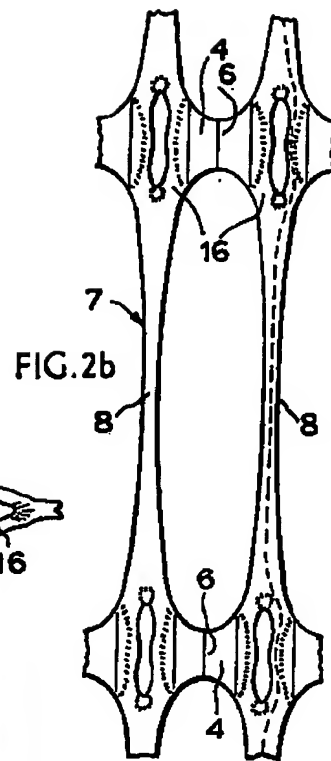
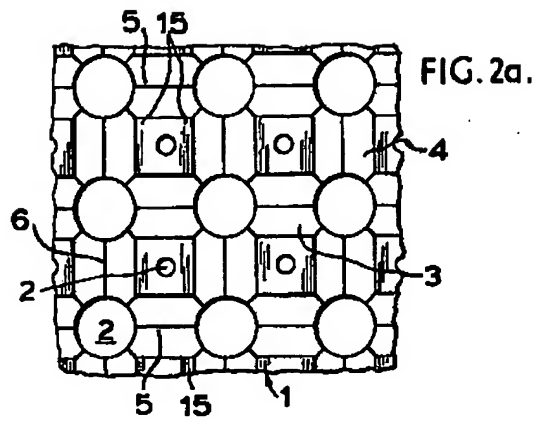


FIG. 1e.



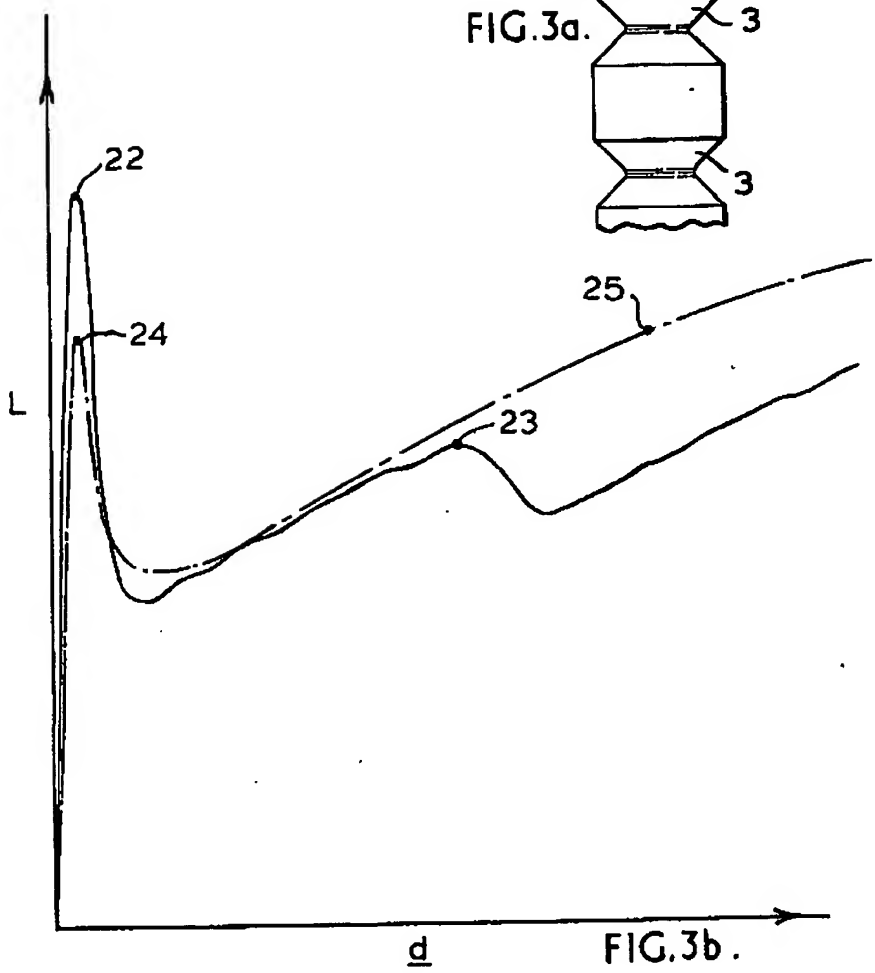
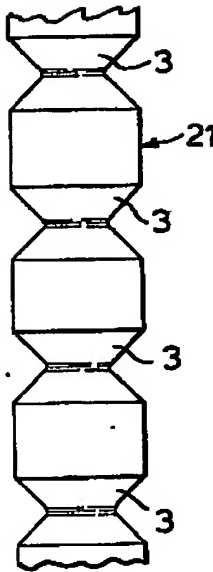
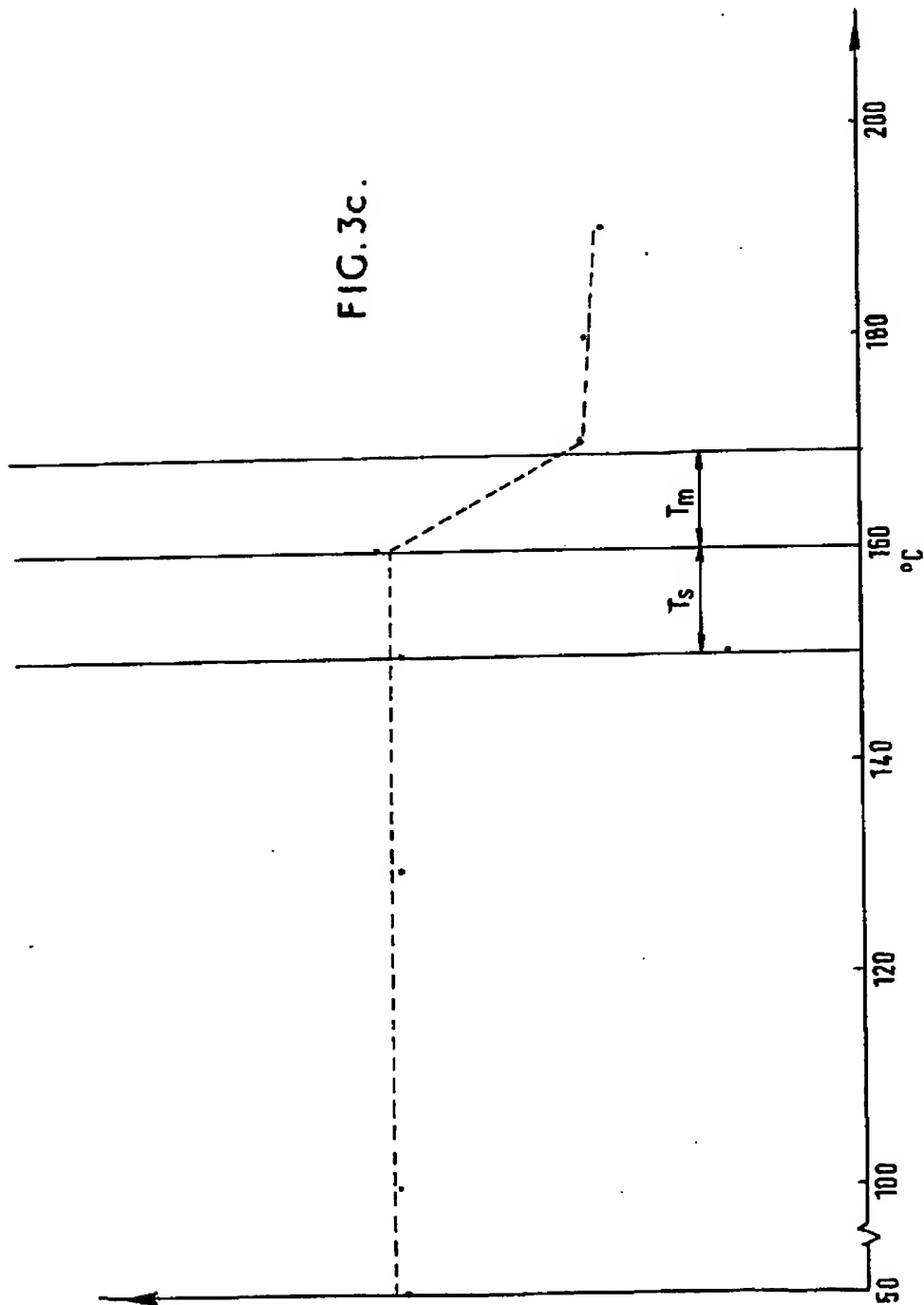
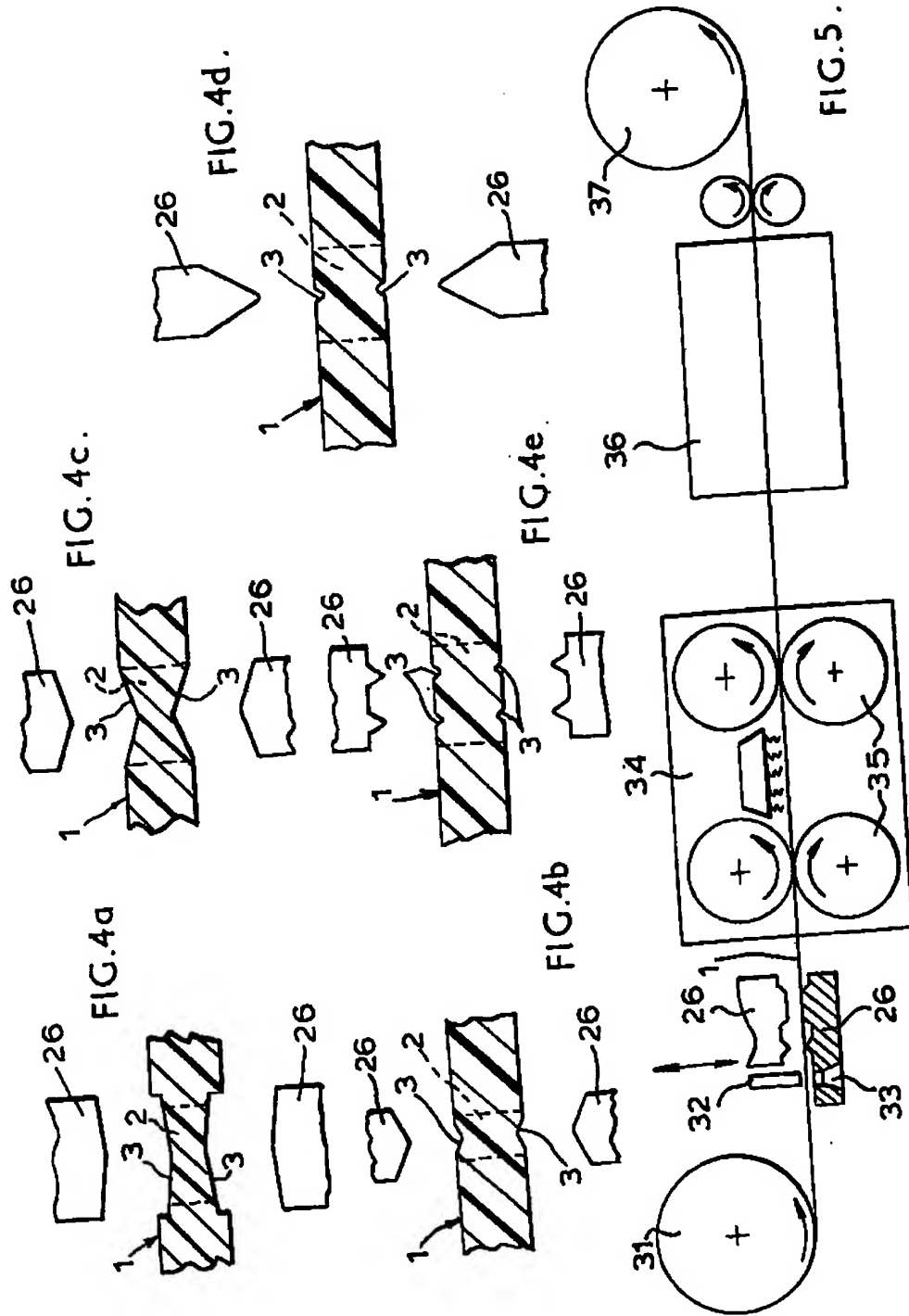


FIG. 3c.





SPECIFICATION

Molecularly orientated plastics material

5 *Background of the Invention* 5

The present Invention relates to a method of stretching plastics material having a pattern of holes or mesh openings to form molecularly orientated strands from zones (called "strand-forming zones" herein) of the plastics material. In some cases, the whole of the plastics material can be stretched out to form orientated strands. The holes may not penetrate right through the plastics material or the mesh openings may contain membranes, if desired. 10

The method of the Invention has been found to be generally applicable, for instance to stretching integrally extruded mesh structures, e.g. those produced as described in GB 836 555, GB 969 655 or GB 1 250 478. The Invention is more particularly applicable to methods of producing integral plastics material mesh structures by stretching starting materials having a pattern of holes which can have been formed for instance by punching. Examples of such methods are described in for instance GB 2 031 833A, GB 2 034 240A, GB 2 035 191B, GB 2 059 868A, GB 2 073 090B, GB 2 096 531A, GB 2 108 896A, and GB 82 19477. In all these methods, strands are formed from strand-forming zones of the starting plastics material. Nonetheless, the Invention was made in connection with producing biaxially-stretched materials in accordance with GB 2 035 191B, and will mainly be described in relation to GB 2 035 191B, the mesh structure produced being called "biax Square Mesh" herein for convenience. 20

The standard way of manufacturing biax Square Mesh is to MD (machine, i.e. longitudinal, direction) stretch using nip rolls, relax 5 to 10%, TD (transverse direction) stretch on a stenter, and relax 5 to 10%. On the stenter, there will be a large number of mesh openings across the width. It was observed that the TD stretching of the mesh openings or TD strands was not regular. As most of the initial increase in width was due to only a few strands stretching, there was very rapid stretching of those strands. In extreme cases, the strands could fibrillate and/or rupture. However, apart from the uneven appearance of the final product, less extreme cases could still cause grave disadvantages; on the first (MD) stretch, a slightly different penetration into the bar or a slightly different amount of penetration across the bar could greatly change the junction formed after the second (TD) stretch: if the increased penetration caused the junction to stretch before the strands in the second stretch, a much weaker and radically different junction would be formed. Similar differences occurred when the second stretch was MD; as the stretch length cannot be very short in practice, there is always a number of aligned strands stretching at the same time. Such differences, though not so marked, were also apparent when making uniaxially-stretched structures. 25

In general terms, more difficulties were experienced with polypropylene (PP) than with high density polyethylene (HDPE), but the differences were apparent with HDPE. 30

The Invention

The present Invention provides methods as set forth in Claim 1 or 21 and plastics material as set forth in Claim 22. The remaining Claims set forth preferred features of the invention.

It has been found that by forming the depressions without material removal (i.e. without abstracting material from the structure as a whole), a much more regular structure can be formed. In a measurement of the mesh pitches in the TD, after stretching TD in a stenter, a prior PP biax Square Mesh product had a mesh pitch variation (maximum to minimum) of about 45% whereas a biax Square Mesh product in accordance with the Invention had a variation of about 5%. In effect, when the strand-forming zones are being stretched in a stenter, there is a controlled, repeatable progression; the orientation usually begins in the lateral zones of the web and gradually works towards the centre, this being related to the natural stress pattern imposed by a stenter; one should apply sufficient stretch to achieve reasonable uniformity. The rate of strain during transverse orientation becomes more regular from mesh to mesh. The effect of this equalising of strain rate can ensure that the tensile strength of all the meshes is nearly the same. 40

The reasons for this are not well understood. It is believed that by forming the depression below the melting range, some molecular yielding occurs and there is some pre-orientation of the plastics material in the strand-forming zones, in particular in the deepest part at least of the depression. Microscopic examination under polarised light has indicated some attenuation of the spherulite structure in the direction at right angles to the axis of the depression; there is also some birefringence, signifying some orientation in the same direction. It is believed that the pre-orientation effect is the most important effect. However, there is an indent effect, i.e. predetermining the place where orientation should begin. In addition, the accurate formation of depressions can reduce the variations in thickness which would otherwise occur in the strand-forming zones due to variations in thickness in commercially available plastics material sheets. 45

The yield and draw curves are altered, being made much more regular with a lower yield point (yield load); the yield loads can be greatly reduced, particularly for PP. This reduction can be as high as 30%. There is however very little effect on the tensile strength of the final product. It is believed because no plastics material is actually removed and forming the depression has an effect similar to that which occurs on stretching. The cross-sectional size of the strand in the final product is not substantially altered. 50

The Invention enables stretching machine power to be reduced because the yield loads are smaller. In addition, as the stretching is more regular and very high strain rates can be eliminated, through-put or 55

overall speed of production can be greater. Thus with PP it has been found possible to stretch at a rate of 2000% minute, and stenter through-put speeds of 9 metres/minute have been achieved, expected speeds being as high as 20 metres/minute or more.

A greater degree of control of mesh sizes or strand lengths can be effected with PP since the draw load exceeds the yield load at much lower orientation ratios; if it were desired to have a mesh of a smaller size, the range of orientation ratio capable of producing regular structures would allow this to be achieved.

The advantages of forming the depressions to produce improved structures during TD stretching can also be extended to forming the depressions to produce more regular MD stretched material with similar reductions in yield loads and subsequently lower machine power requirements.

All or most plastics materials have no precise melting point: they have a melting range and a softening range, the ranges not being very precisely definable and overlapping. For instance, the softening and melting ranges may be about 118-128°C and 122-138°C for HDPE and 150-160°C and 160-168°C for PP. It is believed that in theory, the depressions could be formed at a temperature close to, e.g. within about 10°C or 15°C of, the lower limit of the melting range. At higher temperatures, material would merely be displaced, in effect reducing the cross-sectional area of, and weakening, the eventual strand. It is more convenient to form the depressions at lower temperatures. In practice, this means that the preferred temperature is at or substantially below the orientation (stretching) temperature (normally about 100°C for HDPE and 110-130°C for PP) or at or close to the ambient temperature, say 15 or 20°C. There is however a danger that some plastics materials, particularly PP, may shatter if depressions are formed rapidly at low temperature, giving a practical lower limit for mass production using e.g. PP; for instance, the depressions could be rolled into PP at 10°C, but it would be advisable to have a minimum temperature of 20°C if the depressions are pressed in at high speed. GB 1 281 151, FR 1 601 073 and GB 900 914 show the formation of depressions or necks, but they are formed in the molten plastics material and the effect of the present invention is not achieved.

It is preferred that the deepest part of the depressions are substantially at the narrowest parts of the strand-forming zones, but this is not essential and great precision is not usually practicable or necessary - for instance there may be a plurality of depressions in a strand-forming zone, spaced in the direction of stretch. As long as the depressions are not too wide a part of the strand-forming zone, the strand-forming zone will begin to orientate at the depression(s), which is satisfactory.

A wide variety of shapes of depressions can be used, even depressions which do not extend right across the strand-forming zones and are for instance conical. However, the preferred depressions are wedge-shaped, e.g. with the apex of the wedge extending substantially at right angles to the stretching direction; slight radiussing would be applied to the base of the wedge-shaped depression, to stop the tool cutting the plastics material. Alternatively, rounded-section depressions could be used, e.g. a part-circular cylindrical depression with the axis extending substantially at right angles to the stretching direction. In general, with a tool whose cross-section taken parallel to the stretching direction is substantially constant across the width of the tool (direction at right angles to the stretching direction) and presenting opposite, inclined faces in the stretching direction, there is very little movement of the plastics material at right angles to the stretching direction and the orientation caused is most intense at the bottom of the depression. It is preferred that the depressions should extend for the whole length of the holes on either side of the strand-forming zones, though in practice the depressions may be smaller or shorter; the advantage of equating the extent of the depression to the width of the adjacent hole is that on stretching orientation progresses smoothly from the centre of the strand to the junction region. It is possible however to have the depressions bounded by steps substantially at right angles to the faces of the plastics material, the steps also extending at right angles to the stretching direction; this would tend to prevent orientation proceeding beyond the depressions.

The stretching behaviour can be altered by altering the depth of the depressions. It is believed that the depth, rather than the length, of the depression, has the greatest effect.

In practice, the depressions would be formed on the faces of the plastic material. However, at least in theory, it would be possible to form the depressions on the side edges of the strand-forming zones.

The axis of the depression, e.g. the direction in which the base of the wedge extends, is preferably at right angles to the direction in which the strand-forming zone is stretched, or more generally at right angles to the direction of stretch of the starting material as a whole. Thus with a diamond structure such as that of GB 2 034 240A, the axes of the depressions can be at right angles to the direction of stretching the starting material as a whole even though the strand-forming zones extend at an angle to said direction of stretch. Depending on the product to be formed, the axes of the depressions can extend in the TD and/or in the MD.

It is preferred to form the depressions before any stretching, but the strand-forming zones of a second stretch could be formed with depressions after the first stretch.

Some problems would arise because forming the depressions causes a slight increase in MD or TD dimension, possibly 0.5% overall. However, the depressions can be formed by rolling them in, whether in the MD or TD, before or after punching in the case of punched starting materials; pairs of rolls can be used, with the form (corresponding to the depressions) extending around the whole periphery of one or both rolls - this is most suitable for forming MD depressions, and if TD depressions are rolled in, depressions can be formed on the selvages by nipping them with registering (out of mesh) cogs.

Alternatively, the depressions can be formed by straight pressing. The preferred procedure when forming holes in the plastics material by punching, is to press in the depressions during the same press cycle, e.g. as the press ram approaches bottom dead centre; the depressions are thus formed whilst the ram is travelling

at its slowest speed, reducing the possibility of the plastics material being damaged by high impact loads. This can be done for TD and/or MD depressions. The depressions will be formed in a part of the starting material adjacent to the punched hole.

If there are selvages, it is useful to form the TD depressions on the selvages in addition to the body of the material as this helps the selvages behave in the same way as the remainder of the sheet and not distort the sheet. The selvedge would no longer be a wide strip of oriented material of constant thickness but would have an undulating thickness profile with high orientation in the depressed area and a much lower orientation in line with e.g. TD bars. The effect of such a selvedge can be three fold. Firstly - by treating the selvedge in the same way as the body of the structure the tendency to bow forward in the centre of the web during MD stretching will be greatly reduced. Secondly - the selvedge would have the raised sections directly in line with e.g. the TD bar which is to be oriented: therefore on a stenter, the stenter clip would be gripping to maximum effect in the most advantageous position. Lastly - since the raised portions of the selvedge would have much less orientation, the tendency for the selvedge to split or crack would be much less.

Preferred Embodiments

The invention will be further described, by way of example, with reference to the accompanying drawings, in which:-

- Figure 1a* is a plan view of a starting material in accordance with the invention;
 - Figure 1b* is an isometric view of the starting material of *Figure 1a*;
 - Figure 1c* is a section along the line I-A-I-A of *Figure 1a*;
 - Figure 1d* is a plan view of the mesh structure formed by stretching the starting material of *Figure 1a* uniaxially (the scale is about half that of *Figures 1a* to *1c*);
 - Figure 1e* is a plan view of the mesh structure formed by stretching the mesh structure of *Figure 1d* along a second axis at right angles;
 - Figures 2a* to *2c* correspond to *Figures 1a*, *1d* and *1e* but show a different starting material and mesh structures;
 - Figure 3a* is a plan view of a test strip;
 - Figure 3b* is a load/extension graph;
 - Figure 3c* is a graph of peak load against depression temperature;
 - Figures 4a* to *4e* show depression shapes, as seen in section along the line IV-IV in *Figure 1a*, on a larger scale; and
 - Figure 5* is a schematic side view of plant for carrying out the invention.
- In the respective *Figures*, the lines ("profile shading") which indicate the profile of the structure extend up and down the slope, following the line of maximum gradient, i.e. at right angles to conventional contour lines.

Figures 1a to 1e

The uniplanar starting material 1 of *Figure 1a* has a pattern of holes 2 whose centres lie on a notional, substantially square or rectangular grid. As shown in *Figure 1a*, depressions 3, 4 are formed by pressure (no material removal) in the strand-forming zones 5, 6 which are to be stretched. The way of stretching the starting material 1 is known and is also explained in GB 2 035 191B. During orientation, the plastics material is maintained approximately at a uniform temperature, a water bath being effective for this purpose as it removes adiabatic heat generated during stretching. In the first stretch, a uniplanar, uniaxially stretched structure 7 (*Figure 1d*) is formed. The stretching force is applied at the same time to a plurality of first strand-forming zones 5 in series; orientation begins at the indents of the strand-forming zones 5 and the zones 5 are stretched out into orientated strands 8 which are interconnected by substantially parallel bars 9. Each bar comprises a succession of alternate notional zones, namely zones 10 between and interconnecting the ends of aligned strands 8 and the second strand-forming zones 6 between the zones 10. As indicated by the profile shading in *Figure 1d*, the orientation of the strands 8 proceeds at least as far as the notional tangent line 11 indicated in *Figures 1a* and *1d*.

In the second stretch, the structure 7 of *Figure 1d* is stretched in a second direction at right angles to form a uniplanar, biaxially-stretched structure 12 (*Figure 1e*). The stretching force is applied to a plurality of the second strand-forming zones 6 in series; orientation begins at the indents of the second zones 6 and the second zones 6 are stretched out into orientated strands 13. The structure 12 is in the form of a generally rectangular grid of orientated strands 8, 13 and orientated junctions 14 therebetween, the profiles of the junctions 14 being indicated by the profile shading.

It will be seen that the holes 2 are radlussed squares with their diagonals parallel to the stretching directions, defining wedge-shaped indents in the side edges of the strand-forming zones 5, 6; this provides a pronounced indent effect in addition to that of the depressions. An advantage of these holes 2 is that on the first stretch the stress applied to the strands 8 is dispersed and not directed narrowly straight across the bar 9; this causes the distance of penetration of orientation into the bar 9, or the amount of penetration across the bar 9, to be controlled, and in turn causes the penetration to be more regular across the mesh structure 7.

Figures 2a to 2c

These Figures correspond to Figures 1a, 1d and 1e above, modified in accordance with the method of GB 2 098 531A, and need not be described in detail. Figures 2a to 2c illustrate that it is not necessary to form the depressions in all strand-forming zones (though manually all corresponding strand-forming zones would be formed with like depressions). No depressions are specifically formed in the zones 15 that form the short strands or legs 16 though there is some tapering of an edge. The width of the main strand-forming zones 3 is chosen in relation to the width of the zones 15 such that the zones 3 orientate first, when it is found that the zones 15 orientate reasonably regularly.

Figures 3a, 3b and 3c

Test strips 21 were cold profiled at the sides (with material removal) and correspond to a strip down the starting material 1 of Figure 1a between the dashed lines 21' without the depressions 14. The test strips 21 had a maximum width of 16 mm, the remainder of the details being as for Figure 4c below (see Table 2 below), as appropriate. Orientation tests were carried out at 110°C with test strips with planar faces, and with test strips formed at 110°C with the depressions 3, measuring the load (L) against extension (d). The graph of Figure 3b was drawn.

Even with the test strip 21 without the depressions 3 (full line in Figure 3b), some physical change occurs in the strand-forming zones when the load is applied. However, one of the strand-forming zone yields first (point 22 in the graph), orientation occurs and the load decreases. The load then increases in rounded steps to a new maximum 23 (late start to orientation in one or more strand-forming zones), decreases as the further zone(s) begin to orientate, and so on.

When the depressions 3 are present (dash-dot line in Figure 3b), the strand-forming zones all begin to orientate at the same time (point 24, about 20% lower than point 22), and there are no further maxima, a smooth curve being followed. The draw load exceeds the yield load at point 25.

With HDPE, there was little reduction of the yield load (therefore little reduction in power requirements) but the draw curve was smoother, indicating a regular stretching of the meshes in series.

Using the same test pieces 21, depressions were then formed at various temperatures. Orientation was again carried out at 110°C. The tensile tests were then carried out at ambient temperature (20°C). Details of the tests are set out in Table 1 below, and Figure 3c is a graph of the peak load on the product against the temperature at which the depressions were formed. The vertical lines indicate the softening range (T_s) and the melting range (T_m). Below 170°C, the test pieces were heated up in an oven to the temperature specified; however, from 170°C, the depressions 3 had to be formed using a hot grooving tool to heat the plastics material rather than using a hot test piece. In spite of the difference in procedure, there is a clear indication of a change in behaviour over the melting range. This is believed to be the result of flowing material in a molten state away from the centre of the depression, at temperatures of 170°C and above, as opposed to carrying out a small amount of molecular orientation at temperatures of 160°C and below.

TABLE 1

	Depressions formed at °C	Orientation Yield Load	Product Peak Load	Strand Tensile Strength N/mm ²	
40	50	124.0	157.5	447	40
45	100	125.5	158.2	470	45
	125	125.0	157.5	462	
	150	133.0	157.0	452	
50	160	120.0	162.0	453	50
	170	138.0	123.0	403	
55	180	135.0	122.0	394	55
	190	130.5	119.0	395	

Figures 4a to 4e

Table 2 below gives details of various examples of the depressions 3 of Figures 4a to 4e. Registering depressions 3 of the same depth were formed on opposite faces of 4.5 mm thick PP; the ends of the holes 2 are indicated with dashed lines. The base of each depression 3 is approximately coincident with the centre lines of the holes 2, except for Figure 4e. For different thickness materials, the depressions 3 can be altered proportionally. The tools 28 are indicated; Figure 4b shows that the same tool could be used to make depressions of differing lengths and depths.

TABLE 2 (measurements in millimetres)

	F r m	Length f each	Depth of each	Ratio of combined depth to material thickness	Inclination of base facets	Height of step	Pitch of twin	Length of hole	
5									5
	Fig. 4a	10	0.8	28%	3°	0.34	—	8	
10	Fig. 4b	1.6	0.4	18%	26°	—	—	4	10
	Fig. 4b	1.0	0.45	20%	26°	—	—	4	
15	Fig. 4b	2	0.5	22%	26°	—	—	4	15
	Fig. 4b	2.2	0.55	24%	26%	—	—	4	
	Fig. 4c	8	0.55	24%	12°	—	—	8	
20	Fig. 4d	0.52	0.45	20%	60°	—	—	8	20
	Fig. 4e	0.35	0.3	13%	60°	—	4	8	

25 It will be seen that the depressions 3 can be longer than the holes 2 (Figure 4a), shorter than the holes 2 (Figures 4b) or the same length as the holes 2 (Figure 4c). Figures 4d and 4e show that the sides of the depression 3 can be steeper to reduce the force required, and preferred angles are in the range of about 50° to 70°, the end of the tool 26 being radiused to avoid a cutting edge; it is found that the product is substantially the same. Figure 4e shows that more than one depression 3 can be formed in a strand-forming zone 5; if desired, the remote edges of the twin depressions could be aligned with the ends of the hole 2. In one direction, orientation will run along the strand-forming zone 5 until it meets the orientation from the other depression 3 — in the other direction, orientation will pass into or be impeded by the bar 9 or junction 14 in the normal manner.

30 Expressed as a percentage of the thickness of the undepressed zones of the plastics material, the depth of a depression 3 on one face only (i.e. with no registering depression) or the combined depths of registering depressions 3 on opposite faces, is preferably less than about 40%, more preferably less than about 25% the percentage is preferably more than about 10%, possibly more than about 20%.

Though only the depressions 3 are illustrated in Figures 4a to 4e, the depressions 4 could be shaped likewise.

40 Figure 5

Figure 5 shows plant for the biaxial stretching of punched plastics material sheet, generally as in GB 2 035 191B. The sheet is unwound from a reel 31 and passed between a line of reciprocating punches 32 and dies 33. The punch beam and the die beam carry tools 26 for forming depressions 3 as in Figure 1a, adjacent the bottom dead centre of the movement of the punch beam. The starting material 1 is then heated in an enclosure 34, stretched MD by differential rolls 35, stretched TD on a stenter in a heated enclosure 36, cooled, and wound on a reel 37. In each direction, the stretching force was applied to a plurality of the strand-forming zones 5, 6 at the same time. If desired, the MD stretched material could be cooled and wound on a reel directly after MD stretching, and later unwound for TD stretching.

50 CLAIMS

1. A method of stretching plastics material having holes or mesh openings to form orientated strands from strand-forming zones of the plastics material, and including the step of forming depressions in at least some of the strand-forming zones without material removal when the plastics material is at a temperature below the lower limit of its melting range, prior to stretching the respective strand-forming zones.

2. The method of Claim 1, wherein there is a plurality of the strand-forming zones in series in the stretching direction to which a stretching force is applied at the same time.

3. The method of Claim 1 or 2, wherein said temperature is substantially below the temperature at which the strand-forming zones are stretched.

4. The method of Claim 1 or 2, wherein said temperature is at or close to ambient temperature.

5. The method of any one of the preceding Claims, wherein the depressions are formed with a tool whose cross-section taken parallel to the stretching direction is substantially constant across the width of the tool, and which presents opposite, inclined faces.

6. The method of any one of the preceding Claims, wherein the depressions are wedge-shaped, the apex

of the wedge extending substantially at right angles to the direction in which the respective strand-forming zones are to be stretched.

7. The method of any one of the preceding Claims, wherein a respective depression is in a strand-forming zone between two holes or mesh openings which have the same length in the direction of stretch of the strand-forming zone, the depression extending substantially for the whole length of the holes or mesh openings but not substantially further. 5
8. The method of any one of Claims 1 to 6, wherein a respective depression is in a strand-forming zone between two holes or mesh openings which have the same length in the direction of stretch of the strand-forming zone, the depression extending for substantially less than the length of the holes or mesh openings. 10
9. The method of any one of the preceding Claims, wherein the deepest part of a respective depression is substantially at the narrowest part of the strand-forming zone, as measured at right angles to the direction in which the strand-forming zone is to be stretched. 10
10. The method of any one of the preceding Claims, wherein the depressions are bounded by steps substantially at right angles to the faces of the plastics material, the steps extending substantially at right angles to the direction in which the respective strand-forming zones are to be stretched. 15
11. The method of any one of the preceding Claims, wherein not more than one depression is formed in a strand-forming zone.
12. The method of any one of Claims 1 to 10, wherein a plurality of depressions, spaced apart in the direction of stretching the respective strand-forming zone, are formed in a strand-forming zone. 20
13. The method of any one of the preceding Claims, wherein the plastics material is biaxially-stretched in a continuously-operating plant, one stretch being effected in the machine direction and the other stretch being effected in the transverse direction, and the depressions being formed in at least those strand-forming zones which will stretch in the transverse stretch direction.
14. The method of any one of the preceding Claims, wherein the starting material is formed by punching holes in a plastics material sheet, the depressions being formed generally at the same time as the punching in an adjacent part of the starting material. 25
15. The method of any one of the preceding Claims, wherein the depth of a depression on one face only of the plastics material, or the combined depths if there are registering depressions on opposite faces of the plastics material, expressed as a percentage of the thickness of the undepressed zones of the plastics material, is about 40% or less than 40%. 30
16. The method of Claim 15, wherein the percentage is about 25% or less than 25%.
17. The method of any one of the preceding Claims, wherein the depth of a depression on one face only of the plastics material, or the combined depth if there are registering depressions on opposite faces of the plastics material, expressed as a percentage of the thickness of the undepressed zones of the plastics material, is about 10% or more than 10%. 35
18. The method of any one of the preceding Claims, wherein there are registering depressions on opposite faces of the plastics material, and of substantially the same depth.
19. The method of any one of the preceding Claim, wherein, in the side edges of the respective strand-forming zones in which said depressions are to be formed, said holes or mesh openings define wedge-shaped indents. 40
20. The method of Claim 19, wherein said holes are radiussed squares with a diagonal parallel to the direction in which the respective strand-forming zones are stretched.
21. A method of stretching plastics material, substantially as herein described with reference to, and as shown, in, any one of Figures 1a to 1d, Figures 2a to 2d, Figure 4a, Figure 4b, Figure 4c, Figure 4d, Figure 4e, or Figure 5 of the accompanying drawings, or with reference to any one of the examples of Table 2. 45
22. Plastics material which has been stretched by the method of any one of the preceding Claims.